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THEORY OF SURFACE IONIZATION ON GLOWING METALS

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THEORY OF SURFACE IONIZATION ON GLOWING METALS

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A. I. Ansel'm

An attempt is made to compile a kinetic theory for surface ionization on glowing metals. The Sommerfeld model of a metal provides the basis of the method employed.

The phenomenon of surface ionization is as follows. Neutral /329* atoms of alkali metals, falling on a glowing surface of a metal (tungsten, molybdenum, tantalum) are partly volatilized from it with the ionized atoms. This phenomenon was discovered experimentally and studied for cesium atoms which were volatilized from the surface of glowing tungsten in a study by Kingdon and Langmuir (Ref. 1) and Becker (Ref. 2). Surface ionization of rubidium and potassium, on pure and oxidized tungsten, was observed by Killion (Ref. 3).

Finally, E. M. Ayer (Ref. 4) observed the dependence of potassium atom ionization on the nature of the glowing metal (tungsten, tantalum, and molybdenum). A thermodynamic theory for surface ionization was developed by Langmuir and Kingdon (Ref. 5). It led to the following simple relationship

$$\frac{\nu_p}{\nu_a} = \frac{1}{2} e^{\frac{\varepsilon(\varphi - V_i)}{KT}} \qquad (1)$$

where ν_p and ν_a are the number of positive ions and neutral atoms which are volatilized from 1 cm^2 of surface in one second; ε - the electron charge; ϕ - the work function of the metal, on whose surface atoms of an alkali metal are ionized, with the ionization potential of V_i K = $1.36 \cdot 10^{-16}$ erg/degree (Boltzmann constant); and T - absolute temperature of the ionizing surface.

It may be seen from (Ref. 1) that the nature of the phenomenon depends essentially on whether $\phi > V_i$ or $\phi < V_i$. All of the experimental works cited above pertain to the first case.

An article recently published by Morgulis (Ref. 6) investigated the surface ionization of sodium atoms on tungsten (V_i = 5.12 volts and ϕ = 4.52 volts), which pertained to the second case: $\phi < V_i$.

In all of the articles cited above, which generally provide excellent substantiation of formula (1), primarily the temperature dependence of the ratio ν_p/ν_a was studied, and not its absolute value.

* Numbers in the margin indicate pagination in the original foreign text.

In this report, we shall try to compile a kinetic theory for surface ionization.

Our statements are based on the Somerfeld model of a metal (Ref. 7) with free electron gas and with a work function of

$$\varphi \quad W_a \quad W_i, \tag{2}$$

where W_a and W_i are, respectively, the "outer" and "inner" work function. The reflection of atoms from the surface of a glowing metal was regarded as consecutive condensation and volatilization, as was done by Langmuir. According to the theory of Frenkel (Ref. 8), the mean life time of an atom in an adsorbed state is

$$\tau = \tau_0 e^{\frac{u}{KT}} \tag{3}$$

where τ_0 is the period of the thermo-oscillation of an adsorbed atom, u /330 is the adsorbtion heat, and T is the absolute temperature. Employing the data presented by Taylor and Langmuir (Ref. 9) for u on the volatilization of cesium from tungsten, and assuming that $\tau_0 \cong 10^{-13}$ seconds and $T \cong 2500°$ K, we obtain the following for the lower limit

$$\tau \cong 10^{-9} \text{ seconds} \tag{4}$$

It should be pointed out that in the majority of cases τ reaches very high values. The following considerations are based on the assumption that the energy level V_i, of a valent electron of an adsorbed atom, is displaced very slightly, and extends in the surface field of the metal. This assumption may only be based on the subsequent agreement between the conclusions of the theory and experiment, since we know too little about the nature of the metal surface. On the other hand, we shall assume that the isoenergetic (we shall only investigate the most probable ones) transitions of an electron from the valent level of an adsorbed atom in the metal (without taking into account the statistically free electrons), and vice versa, are very probable during the time τ.

Employing the uncertainty relation of Heisenberg $\Delta E \Delta t \cong h$, we may show that the two following assumptions do not contradict each other: the retention of the discreet, unperturbed energy level V_i in the adsorbed atom, and its small life time in the neutral state. Simple computations show that the inequalities must be together fulfilled simultaneously: $\Delta t \ll 10^{-9}$ seconds and $\Delta t \gg 10^{-15}$ seconds. If an equilibrium state is established during the time τ, between the valent electron of an adsorbed atom and the free electrons of the metal, we may then regard the level V_i as one of the possible (additional) states for free metal electrons. According to Fermi (Ref. 10), the probability that the state with the total energy E is not occupied by an electron is proportional to

$$1 - \frac{1}{\frac{1}{A} e^{\frac{E}{KT}} + 1} = \frac{1}{1 + Ae^{-\frac{E}{KT}}} \tag{5}$$

It is apparent that the number of positive ions ν_p which are volatilized from 1 cm^2 of glowing metal surface is proportional to the probability that the state of the valent electron in an adsorbed atom is free, i.e.,

$$\nu_p = \frac{C}{1 + Ae^{\frac{\varepsilon V_i}{KT}}}, \tag{6}$$

since the total energy of the valent electron $E = -\varepsilon V_i$.

Since the electron gas in the metal is degenerate for the very high temperatures which may be reached during experiments, we then have

$$\lg A = \frac{E_m}{KT}, \tag{7}$$

where E_m is the total energy of a free electron having the maximum kinetic energy εW_i, i.e.,

$$E_m = -\varepsilon W_a + \varepsilon W_i = -\varepsilon (W_a - W_i) = -\varepsilon\varphi. \tag{8}$$

It follows from (6), (7), and (8) that

$$\nu_p = \frac{C}{1 + e^{\frac{\varepsilon (V_i - \varphi)}{KT}}}, \tag{9}$$

where the constant C does not depend on temperature nor on the sign of the difference $V_i - \phi$. In the case of $V_i - \phi < 0$ and $T \to 0$, all of the particles reflected from the metal surface are volatilized in the form of positive ions, i.e., /331

$$\nu_{p_0} = \nu_0, \tag{10}$$

where νp_0 is the number of positive ions in the case of $V_i - \phi < 0$ and $T \to 0$, and ν_0 is the total number of particles which are volatilized from a unit of surface per unit of time. It follows from (9) that

$$\nu_{p_0} = C. \tag{11}$$

On the other hand, in the general case we have

$$\nu_0 = \nu_a + \nu_p \tag{12}$$

Therefore,

$$\nu_p = \frac{\nu_0}{1 + e^{\frac{\varepsilon (V_i - \varphi)}{KT}}} = \frac{\nu_a + \nu_p}{1 + e^{\frac{\varepsilon (V_i - \varphi)}{KT}}} \tag{13}$$

or

$$\frac{\nu_p}{\nu_a} = e^{\frac{\varepsilon (\varphi - V_i)}{KT}} \tag{14}$$

which, within the accuracy of the factor $\frac{1}{2}$, coincides with formula (1).

It must be pointed out that the recently published observations of Copley and Phipps (Ref. 11) on the absolute magnitude of ν_p/ν_a (potassium on tungsten) confirmed formula (14), and not (1).

The contradiction between formula (1), which was derived by a thermodynamic method, and experiment may be explained, from our point of view (which opinion is not shared by the authors cited above) by the fact that the theoretical formula of Nordheim (Ref. 12) is used to derive expression (1) for the thermoelectron emission:

$$\nu_e = \frac{4\pi m_e K^2}{h^3} T^2 e^{-\frac{e\varphi}{KT}}, \qquad (15)$$

where ν_e is the electron flux from 1 cm^2 of surface per one second; m_e is the electron mass; k and h are the Boltzmann and Planck constants. Expression (15) does not agree with experiment (Ref. 13). This yields a value for the factor before T^2 which is smaller by a factor of 2, and which equals $\frac{2\pi m_e K^2}{h^3}$. Up to the present time, this cannot be explained by theory. If we change formula (15), as is required by experiment, the thermodynamic theory leads to expression (14).

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